

# PATENT SPECIFICATION

NO DRAWINGS.

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## COMPLETE SPECIFICATION.

### Improved Anti-Fouling Composition.

We, INTERNATIONAL PAINTS LIMITED, of Grosvenor Gardens House, Grosvenor Gardens, London, S.W.1, a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention relates to anti-fouling paint compositions in which organometallic poisons are chemically bound in the paint vehicle, i.e. the continuous phase of the paint.

This invention is based upon the discovery that a considerable increase in the anti-fouling efficacy of such paints is obtained by using pigments which have an appreciable water-solubility in large quantity by comparison with the quantity of paint vehicle.

The present invention therefore provides an anti-fouling paint comprising (a) a polymer vehicle having organotin radicals chemically combined therein and (b) a water-soluble pigment, the ratio of water-soluble pigment to vehicle being at least 3/1 by weight.

A particularly great increase in antifouling efficiency is obtained if the pigment has a toxicity to marine organisms in its own right. Examples of such pigments are cuprous oxide copper aceto-arsenite, zinc oxide and zinc chromate.

The anti-fouling action is developed to high efficiency if toxic pigments with appreciable water-solubility are incorporated in large quantity by comparison with the quantity of paint vehicle. Thus cuprous oxide and zinc oxide, or blends thereof, are pre-

ferably used at ratios between 3/1 and 5.5/1, pigment/vehicle, by weight.

Anti-fouling paints made on the lines described in the previous paragraph have the advantage over those hitherto known that they remain effective for a long time. The efficacy and life of such a paint exceed those of a comparable paint in which cuprous oxide or zinc oxide is incorporated in a vehicle which contains no chemically combined organometallic poison. Its effective life exceeds that of a paint of comparable poison content containing cuprous oxide or zinc oxide and an organometallic poison such as tri-n-butyl tin oxide which has been ground or stirred into the vehicle. It is considered that these advantages arise directly from the chemical combination of the organo-tin radicals with the polymeric paint vehicle and the high proportion of water-soluble pigment. There is some indication that the chain length of the polymer has an effect on the efficacy of the composition, inasmuch as the antifouling properties are at their best when the molecular weight is lower, and if the molecular weight becomes too high there is a decline in antifouling efficiency. There is, of course, a lower limit below which the mechanical properties of the films are unsatisfactory.

The pigment/vehicle ratios in this Specification are determined by comparing the weight of water-soluble pigment, and the weight of non-volatile paint vehicle, including plasticisers, if present. If non-water-soluble pigment is also present, it is ignored for the purpose of determining the ratio. The organo-tin radicals chemically combined in the polymer may be organo-tin radicals of

formula — $\text{SnR}^1\text{R}^2\text{R}^3$ , where  $\text{R}^1$ ,  $\text{R}^2$  and  $\text{R}^3$  may be the same or different radicals chosen from n-propyl, isopropyl, n-butyl, n-amyl and phenyl radicals. It is especially preferred for  $\text{R}^1$ ,  $\text{R}^2$  and  $\text{R}^3$  all to be n-butyl. The polymer may conveniently be a polymer of a salt of an  $\alpha$ ,  $\beta$ -unsaturated acid and an organo-tin group. Examples of this type of acid are acrylic acid and methacrylic acid, and useful polymers may be made from tri-n-butyl tin methacrylate and tri-n-butyl tin acrylate.

In order to make an anti-fouling paint it is necessary that the paint film, notwithstanding any possible loss of soluble matter into sea-water, shall retain sufficient integrity of film to continue its antifouling activity at least for several months. It has been found that, for instance, a homopolymer of tri-n-butyl tin methacrylate rapidly shrinks and disintegrates when immersed in sea-water. If however, another monomer is co-polymerised with it this disadvantage is overcome and the film remains intact on immersion.

Therefore the polymer is preferably a co-polymer of a monomer containing an organotin radical and another co-polymerisable monomer. Examples of such co-monomers which have been found effective are methyl methacrylate, isobutyl methacrylate and styrene. In such co-polymers the proportion of organo-tin monomer units can be from 20 to 60% by weight.

Co-polymers of, for example, tri-n-butyl tin methacrylate and methyl methacrylate may be made which are hard and tough, and films thereof remain continuous when immersed in water. On prolonged immersion, however, they tend to embrittle, and when used as paint vehicles they may crack. Addition of plasticisers such as di-alkyl phthalates, e.g. di-butyl-phthalate or di-octyl phthalate (i.e. di-2-ethyl-hexyl phthalate) overcomes this defect.

Another method of plasticising the films which may be used instead of, or in addition to, the incorporation of such plasticisers consists of incorporating another co-monomer during the polymerisation. Such co-monomers may be alkyl acrylates and methacrylates, for example, 2-ethyl hexyl acrylate, n-butyl acrylate or n-butyl methacrylate. Such a co-polymerised plasticising component is completely compatible with the film and resistant to the leaching action of water and to any possible migration into a substrate.

An example of a suitable paint vehicle is a co-polymer of tri-n-butyl tin methacrylate, methyl methacrylate and n-butyl acrylate, and additional plasticisers as specified above may be added to this if desired.

Films of such polymers or co-polymers as described above are found to have an appreciable

anti-fouling activity. It is possible that this arises from a hydrolysis of the organo-metallic side-chains, releasing simple organo-metallic salts in a gradual way.

The invention will be further described with reference to the following Examples which are preceded by two comparative Examples not illustrative of the invention.

#### Comparative Experiment 1:

80 gm. tri-n-butyl tin methacrylate and 0.8 gm. benzoyl peroxide were dissolved in 217 gm. toluene, and heated during 20 minutes to 100°C. After 15 minutes at this temperature, 80 gm. methyl methacrylate containing 0.8 gm. benzoyl peroxide were added with stirring, stirring continued and the temperature maintained at 100°C.; after a further 30 minutes 80 gm. methyl methacrylate containing 0.8 gm. benzoyl peroxide were added; and after a further 45 minutes 80 gm. methyl methacrylate containing 0.8 gm. benzoyl peroxide were added, stirring being continued and the temperature controlled at 100°C. throughout. The solution was held at 100°C with stirring for a further 30 minutes, then 217 gm. of toluene was added, and the solution cooled and filtered, some suspended polymer being removed. The solution had a non-volatile content of 38.2% by weight and a viscosity of 8 poises at 25°C.

A film of this resin was laid down on wood, and suspended from a raft in sea-water at a time when animal and vegetable fouling organisms were settling. It was found to possess some antifouling properties.

#### Comparative Experiment 2

118.5 gm. of the resin solution prepared in Example 1 were mixed with 56.2 gm. anatase titanium dioxide pigment, 11.2 gm. dibutyl phthalate and 2.25 gm. toluene, ground in a ball-mill, and thinned with 9.0 gm. toluene. The resulting paint possessed some anti-fouling properties.

#### Example 1:

9.9 parts by weight tri-n-butyl tin methacrylate and 0.6 parts benzoyl peroxide were dissolved in a mixture of 29.7 parts methyl methacrylate, 13.2 parts xylene and 13.5 parts 4-methoxy-4-methylpentan-2-one. The solution was heated to 80°C and held at that temperature for 4 hours with stirring. A further 33.1 parts xylene were added, to reduce the viscosity, and the solution held with stirring for a further 11.5 hours at 80°C. It was then cooled and stabilised by adding 0.01 parts hydroquinone. The viscosity was 120 poises at 25°C and the non-volatile content 39.3% by weight.

26.7 parts by weight of the resin solution prepared as described were mixed with 62.2 parts cuprous oxide, 1.1 parts iron oxide pigment, 2.6 parts di-butyl phthalate and 7.4

parts toluene, ground in a ball-mill and thinned with 150 parts toluene. The resulting paint which had a water-soluble pigment/vehicle ratio of 4.75/1 possessed excellent anti-fouling properties.

**Example 2:**

30.0 parts by weight of the resin solution prepared as in Example 1 were mixed with 20.0 parts cuprous oxide, 40.0 parts zinc oxide and 10.0 parts toluene, ground in a ball-mill and thinned with 10.0 parts toluene. The resulting paint which had a water-soluble pigment/vehicle ratio of 5.1/1 possessed very good anti-fouling properties.

**Example 3:**

236.2 gm. tri-n-butyl tin methacrylate dissolved in 730.5 gm. toluene were stirred in a 3-litre flask and 2.52 gm. benzoyl peroxide added. The solution was heated to 100°C during 20 minutes, and held at that temperature. 781.2 gm. methyl methacrylate, containing 7.81 gm. benzoyl peroxide dissolved in it, were added in three equal portions 15 minutes, 45 minutes and 75 minutes after the tri-n-butyl tin methacrylate solution had reached 100°C, the temperature being held at that level and stirring continued throughout. The mixture was held at 100°C with stirring for 6 hours after adding the final quantity of methyl methacrylate, cooled, and diluted with 890 gm. toluene. The solution has a non-volatile content of 38.8% by weight and a viscosity of 1.8 poises at 25°C.

22.1 parts by weight of the resin solution made as described, 59.0 parts cuprous oxide, 1.0 part iron oxide pigment, 0.5 parts Bentone (Bentone is a Registered Trade Mark), 3.4 parts di-2-ethyl-hexyl-phthalate and 13.5 parts xylene were ground in a ball-mill. The resulting paint which had a water-soluble pigment/vehicle ratio of 4.92/1 possessed excellent anti-fouling properties.

**Example 4:**

21.9 parts by weight tri-n-butyl tin methacrylate, 21.9 parts methyl methacrylate, 0.63 parts benzoylperoxide, 30.1 parts 4-methoxy-4-methyl-pentan-2-one and 25.2 parts xylene were raised to 90°C and held at that temperature with stirring for 22 hours. The viscosity was 70 poises at 25°C and the non-volatile content 41.7% by weight.

27.4 parts by weight of the resin solution prepared as described, 60.0 parts zinc oxide and 12.6 parts toluene were ground in a ball-mill and thinned with 13.0 parts toluene. The resulting paint which had a water-soluble pigment/vehicle ratio of 5.25/1 had very good anti-fouling properties.

**Example 5:**

24.3 parts by weight of the resin solution prepared as in Example 4 were mixed with

62.2 parts cuprous oxide, 1.1 parts iron oxide pigment, 2.6 parts di-butyl phthalate and 9.8 parts toluene, ground in a ball-mill and thinned with 5.0 parts toluene. The resulting paint which had a water-soluble pigment/vehicle ratio of 4.89/1 had excellent anti-fouling properties.

**Example 6:**

8.10 kg. xylene, 7.02 kg. tri-n-butyl tin charged into a stainless steel reaction vessel fitted with stirrer, condenser and water-separator. Stirring was started, a reduced pressure of 25 inches of mercury applied, and the charge heated to 85°C. It was held at that temperature under reflux at reduced pressure with separation of water for 2 hours, and cooled. 9.00 kg. xylene, 2.205 kg. n-butyl acrylate, 6.54 kg. methyl methacrylate and 0.346 kg. benzoyl peroxide were added and the temperature raised with stirring to 90°C. It was held there controlling the temperature by application of reflux at reduced pressure when necessary.

After 2 hours at 90°C, 0.079 kg. benzoyl peroxide and 0.168 kg. xylene were added, and the temperature maintained a further 1 hour. It was then raised to 112°C and the solution was slowly cooled, 0.004 kg. hydroquinone being added during cooling. The solution had a viscosity of 40 poises at 25°C and a non-volatile content of 35.5% by weight.

35.5 parts by weight of the resin solution prepared as described, 38.5 parts of amorphous zinc oxide pigment, 13.0 parts acicular zinc oxide pigment, 0.25 parts Bentone 34 (Bentone is a Registered Trade Mark) and 12.25 parts 90/160 solvent naphtha of coal-tar origin were ground in a ball-mill. The resulting paint which had a water soluble pigment/vehicle ratio of 4.1/1 had very good anti-fouling properties.

**Example 7:**

30.5 parts by weight of the resin solution as described in Example 4, 62.0 parts cuprous oxide, 1.0 part iron oxide pigment, 0.5 parts Bentone (Bentone is a Registered Trade Mark) and 5.5 parts 90/160 solvent naphtha of coal-tar origin were ground in a ball-mill. The resulting paint which had a water-soluble pigment/vehicle ratio of 5.72/1 had excellent anti-fouling properties, but was less satisfactory in painting properties (such as flow) than the preferred paints having a water-soluble pigment/vehicle ratio in the range from 3/1 to 5.5/1.

Various modifications may be made within the scope of the present invention. Thus although the Examples show a solution polymerisation process for preparing the co-polymers, emulsion polymerisation or other polymerisation processes known *per se* for  $\alpha$ ,  $\beta$ -

unsaturated acid monomers might also be used.

The term "water-soluble pigment" as used in this Specification will clearly indicate to those skilled in the art of anti-fouling paints that the pigment is one which is capable of being leached from a paint film into sea water over a period of several months. Thus cuprous oxide, copper aceto-arsenite, zinc oxide and zinc chromate are "water-soluble pigments", whereas titanium dioxide and iron oxide are not.

#### WHAT WE CLAIM IS:—

1. An anti-fouling paint comprising (a) a polymer vehicle having organo-tin radicals chemically combined therein and (b) a water-soluble pigment, the ratio of water-soluble pigment to vehicle being at least 3/1 by weight.

2. A paint as claimed in claim 1 wherein the water-soluble pigment is toxic to marine organisms.

3. A paint as claimed in claim 2 wherein the water-soluble pigment is one or more of cuprous oxide, copper aceto-arsenite, zinc oxide and zinc chromate.

4. A paint as claimed in claim 3 wherein the water-soluble pigment is cuprous oxide or zinc oxide or a blend thereof and is used at a water-soluble pigment/vehicle ratio of from 3/1 to 5.5/1.

5. A paint as claimed in any one preceding claim wherein the organo-tin radical in the polymer is of formula  $-\text{SnR}^1\text{R}^2\text{R}^3$  where  $\text{R}^1$ ,  $\text{R}^2$  and  $\text{R}^3$  (which may be the same or different) are n-propyl, isopropyl, n-butyl, n-amyl or phenyl.

6. A polymer as claimed in claim 5 wherein the organo-tin radical is tri-n-butyl tin.

7. A paint as claimed in any one preceding claim wherein the vehicle is a polymer of a salt of an  $\alpha$ ,  $\beta$ -unsaturated acid and the organo-tin radical.

8. A paint as claimed in claim 7 wherein the acid is acrylic or methacrylic acid.

9. A paint as claimed in any one preceding claim wherein the polymer is a co-polymer of a monomer containing an organo-tin radical and one or more co-polymerisable monomers.

10. A paint as claimed in claim 9 in which the co-polymerisable monomer is methyl methacrylate, isobutyl methacrylate or styrene.

11. A paint as claimed in claim 9 or 10 in which the proportion of organo-tin monomer units in the co-polymer is from 20% to 60% by weight.

12. A paint as claimed in claim 10 or 11 in which the co-polymer is a co-polymer of tri-n-butyl tin methacrylate and methyl methacrylate.

13. A paint as claimed in any of the preceding claims wherein the vehicle contains a plasticizer.

14. A paint as claimed in claim 13 wherein the plasticizer is di-butyl phthalate or di-octyl phthalate.

15. A paint as claimed in claim 13 in which the plasticizer is constituted by a proportion of co-polymerised units within the polymer or co-polymer.

16. A paint as claimed in claim 15 in which the co-polymerised units which exert a plasticizing effect are formed by co-polymerization of 2-ethyl-hexyl acrylate, n-butyl acrylate or n-butyl methacrylate.

17. A paint as claimed in claim 16 in which the co-polymer is a co-polymer of tri-n-butyl tin methacrylate, methyl methacrylate, and n-butyl acrylate.

18. An anti-fouling paint substantially as described herein in any one of the Examples.

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